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TYPE OF PHOSPHORUS-CONTAINING GROUPINGS AND THE OPTICAL CHARACTERISTICS OF COATINGS BASED ON TITANIUM-CONTAINING GLASSES

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The effect of the chemical composition of titanium enamels on the type of phosphate groupings formed and the whiteness of enamel coatings is examined. It established that in glasses with an elevated mass content of glass-forming cations, specifically, about 60% SiO_2, the phosphorus-containing grouping formed binds up to two alkali cations, and for 50% SiO_2 phosphate groupings with one alkali cation are predominately formed.

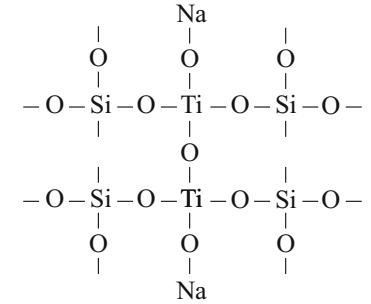
The possibility of obtaining materials with prescribed complex of properties is of considerable interest in materials science. However, this problem is quite complicated, since it requires a reliable knowledge of the structure of the material and the variation of this structure as a function of the chemical composition. If this problem has been solved in part for crystalline substances using the methods of crystal – chemistry to predict and interpret their structure, for amorphous substances, which are distinguished by the disordering of the structural network, such methods do not give positive results, and there are no direct methods for investigating the structure of amorphous substances.

Nonetheless, the problems of studying the structure of amorphous materials can be solved by indirect methods (NMR, IRS, and so forth), which does not always give a unique answer to the questions posed. Evidently, for this reason the method of additivity is widely used to predict the properties of glasses. This method makes it possible to perform a quite accurate calculation of properties such as the CLTE, viscosity, surface tension, and others, but it is completely unsuitable for estimating the whiteness of enamel coatings. This is because the diffuse reflection of enamel coatings is not directly related with the crystalline phases which are formed in them with additional heat-treatment, and structural groupings of the glass undoubtedly serve as the base for them.

We used a collection of different methods to study the structure of boron-free titanium-containing glasses, specifically, determination and analysis of the chemical stability of the glasses with respect to a change of their composition, IRS, XPA of heat-treated crystallized samples, as well as analysis of the change of the brightness and luster of opacified coatings.

The experimental enamel glasses were made in chamotte crucibles in an electric furnace at temperature 1260 – 1280°C followed by granulation of the melts on water. To obtain enamel coatings the frits were milled with an addition of 7 parts by mass of PLG-2 Polozhskoe fireclay, 0.2 parts by mass of KCl, and 45 ml of water. The slips obtained were deposited on primed steel samples, which after being dried were calcined in a muffle furnace at temperature 780 – 840°C for 4 min. The whiteness of the enamel coatings was measured on KTs-3 color computer, and the luster on a GGF-6 luster meter. The absorption spectra were obtained with a Specord-M75 spectrophotometer in the frequency range 1700 – 400 cm^{-1}.

As noted in [1], the crystallization of the titanium-containing glasses is associated with the formation of the structural groupings



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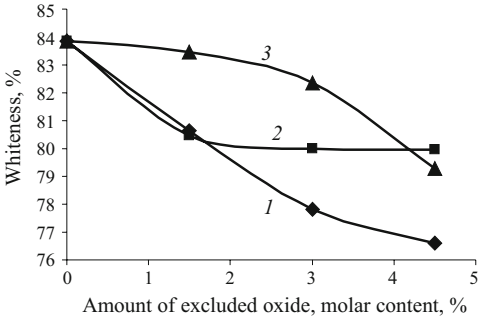
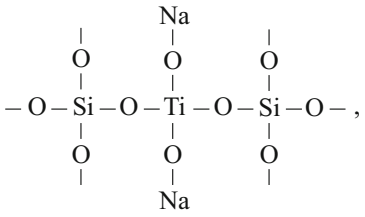


Fig. 1. Effect of the ratio $Na_2O : TiO_2$ [*1*) 0 : 1; *2*) 0.5 : 1; *3*) 1 : 1] removed from the enamel composition on the whiteness of coatings.

and, conversely, the formation of the groupings



(2)

impedes crystallization.

It was determined on the basis of an analysis of the published data [2 – 4] and our own investigations [5 – 7] that B_2O_3, P_2O_5, and Al_2O_3 are the best promoters of the crystallization of glasses because their groupings primarily form with an alkali cation, which is what impedes the formation of the groupings (2). At the same time if a clear relation is observed for B_2O_3 and Al_2O_3 between the crystallization power and the amount of localized alkali oxides ($Na_2O : Al_2O_3$ = 1 : 1, $Na_2O : B_2O_3 = 1/3$), which permits making assumptions about the structure of these fragments, in the investigation of the effect of phosphorus oxide on the crystallization and other properties of titanium-containing glasses it was not possible [7] to establish uniquely the amount of alkali oxides which they localize and the type of structural fragment, even for compositions studied.

In this connection, the goal of our work was to study the effect of phosphorus oxide and type of structural fragment formed on the crystallization of titanium-containing glasses and the whiteness and luster of enamel coatings based on them.

The localization of an alkali cation on aluminum tetrahedra, well-known in the literature [2], and the appearance of a gray hue, which we have established, in titanium-containing enamel coatings with increasing amount of the alkali oxides relative to a definite content of titanium dioxide were confirmed by the fact that we introduced Na_2O and Al_2O_3 in the ratios 1 : 1 and 2 : 1 into boron-free titanium enamel [6]. It was determined experimentally in so doing that the whiteness of the titanium enamels, into which the indicated oxides were introduced in the ratio 1 : 1, remained virtually unchanged. In our view, this shows that their quantity in the alkali-titanate component does indeed remain unchanged on account of the localization of the cations on the aluminum tetrahedron: the ratio of the groupings (1) and (2) is constant. When these oxides were introduced in the ratio 2 : 1, a gray hue appeared in the coatings, which could indicate excess alkali oxides in such enamel.

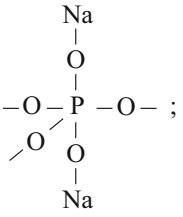
On this basis it appears to be possible to talk about a definite sequence of formation of structural groupings in experimental glasses and to assert that the localization of alkali cations on polyhedral of the cations B^{3+}, Al^{3+}, and P^{5+} is the primary factor. Their quantitative ratio makes it possible to judge indirectly the composition of the grouping formed. To confirm the conclusions that the crystallization power of glasses decreases when groupings (2) form from the composition of the glass 1 (Table 1) we partially excluded Na_2O and TiO_2 in different ratios: 0.5 : 1, 1 : 1, and 0 : 1. When the content of these oxides decreased in the ratios 0.5 : 1 and 0 : 1 the coatings acquired a gray hue. The coatings in which the sodium and titanium oxides were excluded in the ratio 1 : 1 lost a negligible amount of whiteness (Fig. 1) only when

TABLE 1.

Composition	Mass content, %							Amount of excluded oxide, molar content, %	
	SiO_2	Na_2O	TiO_2	Na_3AlF_6	Al_2O_3	P_2O_5	MgO	Na_2O	TiO_2
1	51.24	14.81	14.10	9.40	7.02	1.42	1.96	–	–
2	52.05	15.04	12.80	9.55	7.13	1.44	1.99	–	1.50
3	52.85	15.28	11.45	9.70	7.24	1.46	2.02	–	3.00
4	53.68	15.52	10.06	9.85	7.35	1.49	2.05	–	4.50
5	52.36	14.54	12.87	9.60	7.17	1.45	2.00	0.75	1.50
6	53.49	14.25	11.59	9.81	7.33	1.48	2.05	1.50	3.00
7	54.68	13.95	10.24	10.03	7.49	1.52	2.09	2.25	4.50
8	52.67	14.03	12.95	9.66	7.22	1.46	2.01	1.50	1.50
9	51.15	13.20	11.73	9.93	7.42	1.50	2.07	3.00	3.00
10	55.71	12.32	10.44	10.22	7.63	1.54	2.13	4.50	4.50

4.5% (molar content) TiO_2 was removed from their composition (the mass content of TiO_2 is about 10%), which gives a basis for believing that this method of making a quantitative estimate of the localization of alkali cations on different structural groupings, including on phosphorus polyhedral, holds promise.

In the investigation and analysis of the effect of phosphorus oxide on the properties of titanium-containing enamels, first and foremost, on the whiteness, it was noted that the amount of localized alkali cations per mole of P_2O_5 for glasses with different chemical composition fluctuates in the range 1 – 2% (molar content) Na_2O, which is probably due to the formation of the following groupings in different ratio:



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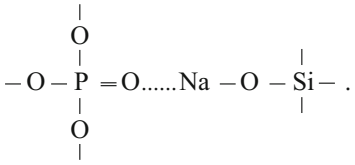

(4)

IR spectroscopy showed an absorption band near 1380 cm^{-1}, characteristic for the P = O (Fig. 2) bond, in the glass 11 (Table 2), where the amount of the localized alkali cations is close to 1. In all other glasses the intensity of this band either decreased (glass 12) or the band was almost completely absent, which could indicate the presence of primarily only the groupings (3) in them. Nonetheless, there is no direct relation with the concentration of phosphorus anhydride in the glasses, and the mass content of P_2O_5 in the glasses for which the absorption spectra are presented is 4.5%.

The effect of the content of titanium dioxide on the formation of the structural fragments based on the phosphorus cation was also studied. For this, TiO_2 and Na_2O were removed in the ratio 1 : 1 from the calculation for exclusion of 2, 4, and 6 wt.% TiO_2 because of the additional SiO_2 introduced (see Table 2), from the composition 13, containing 4.5 wt.% P_2O_5 and where, according to the IR spectra, most of the phosphorus anhydride was in the form of the groupings (4).

Analysis of the optical characteristics showed that in contrast to the composition 1 with a low mass content of phosphorus anhydride (1.42%) the coatings containing about 4.5 wt.% P_2O_5 lost luster and, because of the increase of the viscosity, whiteness (Table 3). This necessitated

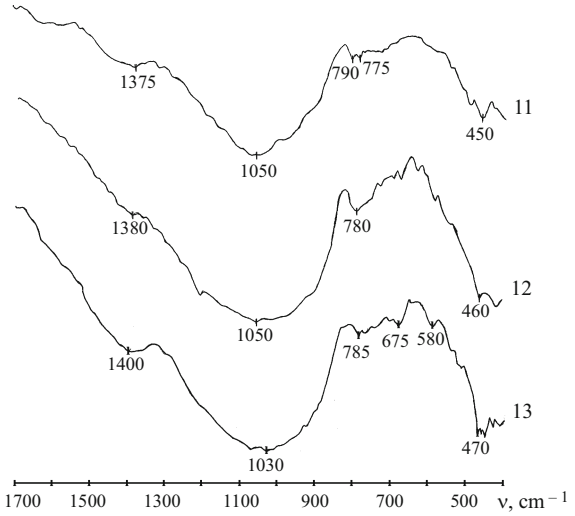

Fig. 2. Infrared absorption spectra of phosphorus-containing glasses. The numbers on the curves correspond to the composition numbers.

spectroscopic studies. It was established that the intensity of the absorption band near 1380 cm^{-1} decreases even though the phosphorus anhydride content remains the same (Fig. 3). This could indicate that the number of groupings (4) decreases and the number of groupings (3) increases. It should be noted that the formation of the groupings (4) is characteristic for glasses with 50 wt.% SiO_2, and the groupings (3)

TABLE 2.

Composition	Mass content, %					
	Na_2O	TiO_2	Na_3AlF_6	SiO_2	P_2O_5	ZrO_2
11	15.0	20.0	10.0	50.1	4.5	0
12	15.0	15.5	10.0	55.0	4.5	0
13	15.0	18.5	10.0	50.5	4.5	1.5
14	13.6	16.7	10.2	53.4	4.6	1.5
15	12.1	14.7	10.5	56.5	4.7	1.6
16	10.5	12.7	10.7	59.7	4.8	1.6

TABLE 3.

Indicator	Composition					
	11	12	13	14	15	16
Whiteness (%) at temperature, °C:						
780	–	–	81.61	77.69	76.84	72.15
810	79.41	67.05	80.85	78.41	78.27	75.18
840	–	–	79.91	78.66	77.29	78.91
Luster (%) at temperature, °C:						
780	–	–	84	43	39	18
810	79	75	86	67	54	32
840	–	–	85	65	61	40

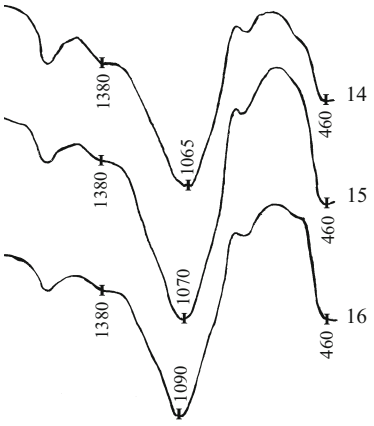

Fig. 3. IR spectra (cm^{-1}) of the glasses. The numbers on the curves correspond to the composition numbers.

are characteristic for glasses with about 60 wt.% SiO_2. This attests to the fact that the number of groupings (3) increases practically linearly as the SiO_2 content in the glass increases from 50 to 60%.

In summary, it has been established that the content of the main network forming agent SiO_2 has a large effect on the type of structural grouping formed with the organizing phosphorus cation, and it was also established that it affects the whiteness, luster, and the degree of fire-polishing of enamel coatings. The formation of the groupings (4) is accompanied by binding of a single sodium cation and the grouping (3) by two alkali cations, which largely prevent the crystallization of titanium dioxide during the heat treatment of glass frits, and as a result of the formation of sodium titanate they impart a gray hue to the coating.

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